Journal of the Korean Physical Society, Vol. 45, No. 2, August 2004, pp. 501∼506

# Temperature Dependence of Raman-Active Modes of $TlGaS_2$ Layered Crystals: an Anharmonicity Study

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(Received 29 March 2004)

The temperature dependence (16 - 300 K) of unpolarized Raman spectra from $TlGaS_2$ layered crystals was measured in the frequency range of 10 - 400 $cm^{-1}$. The analysis of the experimental data showed that the temperature dependencies of the phonon frequencies and linewidths were well described by considering the contributions from thermal expansion and lattice anharmonicity. The anharmonic contribution (phonon-phonon coupling) was found to be due to three-phonon processes. The present work demonstrates that the interlayer Raman mode at 42.6 $cm^{-1}$ shifts toward high frequency as the temperature is raised from 16 to 300 K.

PACS numbers: 78.20.-e, 78.31.-j, 78.30.Hv
Keywords: $TlGaS_2$, Layered crystals, Anharmonicity, Phonon-phonon coupling

## I. INTRODUCTION

Layered semiconductors have become increasingly interesting due to their structural properties and potential applications in optoelectronics. Their quasi-two dimensionality, optical and photoconductive properties, and other features attract investigators in an effort to acquire a better insight into the physics of these compounds. The layered ternary crystal $TlGaS_2$ is an anisotropic crystal whose properties have recently become the subject of extensive research [1–6]. The anisotropy arises from the fact that the bonding within the layers is considerably stronger than that between the layers. In these compounds, van der Waals forces contribute predominantly to the interlayer interaction while the bonding forces within the layers are ionic-covalent. A high photosensitivity in the visible range and a high birefringence in conjunction with a wide transparency range of 0.5-13 $\mu$m make this wide-band-gap crystal useful for optoelectronic applications [7].

Experimental studies of the inelastic light scattering by crystals have provided a great deal of information concerning the optical modes of vibration at the center of the Brillouin zone. For these modes, the frequencies and the widths of the phonon lines are found to vary with temperature. Such a temperature dependence can be understood in terms of the anharmonic character of the lattice vibrations. A large number of papers on the temperature dependences of the frequency and the linewidth of first-order Raman scattering in semiconductors may be found in the literature [8–16]. They show that the Raman shift can be successfully modeled by including the effects of thermal expansion and phonon-phonon coupling.

$TlGaS_2$ belongs to an interesting group of layered ternary semiconductors with the chemical formula $TlBX_2$, where B = Ga or In and X = S or Se. The lattice of $TlGaS_2$ consists of strictly periodic two-dimensional layers arranged parallel to the (001) plane. Each successive layer is rotated by a right angle with respect to the previous one. Interlayer bonding is formed between Tl and S atoms while the bonding between Ga and S atoms is an intralayer one. A view of the crystal structure in the *ac*-plane (*a* is the axis in the [110] direction ) is given in Fig. 1, where the layers are also shown. The fundamental structure of a layer is $Ga_4S_6$ adamantane-like units linked together by bridging S atoms. The Tl atoms are in trigonal prismatic voids resulting from the incorporation of $Ga_4S_6$ polyhedra into a layer. The Tl atoms form nearly planar chains along the [110] and the $[1\bar{1}0]$ directions.

The unit cell of $TlGaS_2$ contains four layers having TlSe ($D_{4h}^{18}$) space group, and the space group of the crystal is $C_{2h}^{6}$. A group-theoretical analysis gives the following set of vibrations at the center of Brillouin zone:

$$\Gamma = 10A_g + 14B_g + 10A_u + 14B_u,$$

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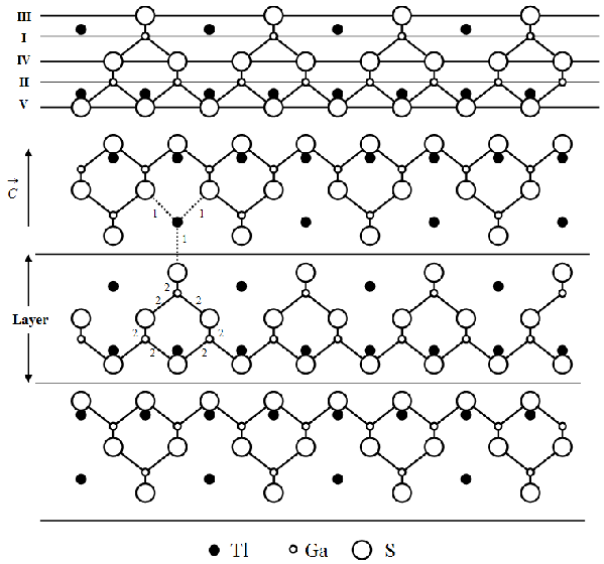


Fig. 1. Projection of the structure in a $TlGaS_2$ crystal as seen from the *ac*-plane. The ones (1) show the interlayer bonding between Tl and S atoms; the twos (2) show the intralayer bonding between Ga and S atoms. From I to V indicate different planes of atoms.

where $10A_g + 14B_g$ are Raman-active modes.

The phonon spectra of $TlGaS_2$ layered crystals have been reported previously from Raman measurements at different temperatures [4,5,17,18]. While much is known about the phonon spectra of $TlGaS_2$, the temperature dependencies of the phonon frequency and the linewidth have not yet been analyzed. The aim of the present study is to measure the frequency and the linewidth (full-width at half-maximum - FWHM) of zone-center optical phonons in $TlGaS_2$ layered crystals by using Raman spectroscopy in the 16 - 300 K temperature range and to compare the experimental results with the existing theories of anharmonicity of lattice vibrations in crystals. We report softening and broadening of the optical phonon lines at the Brillouin zone center with increasing temperature as observed in most other semiconductors. Our analysis and results indicate that the purely anharmonic contributions to the phonon frequency shift and line broadening are due to interactions with phonons of other branches.

## II. EXPERIMENT

$TlGaS_2$ single crystals were grown by using the Bridgman method. The analysis of the X-ray diffraction data shows that the crystalls have a monoclinic unit cell with $a = 1.031$, $b = 1.043$, $c = 1.507$ nm, and $\beta = 99.60°$. Crystals suitable for measurements were obtained by easy cleavage perpendicular to the optical *c*-axis. As-grown $TlGaS_2$ is an p-type semiconductor having indirect band gap with energies of 2.38 and 2.48 eV at 300 and 10 K, respectively [1].

Raman scattering experiments on the $TlGaS_2$ layered crystal were performed in the back-scattering geometry in the frequency range 10 - 400 $cm^{-1}$. A 40-mW He-Ne laser (632.8 nm) was used as the exciting light source. The scattered light was analyzed using a double grating spectrometer with a focal length of 1 meter and a cooled GaAs photomultiplier supplied with the usual photon counting electronics. The Raman line positions were determined within an accuracy of $\pm 0.1$ $cm^{-1}$. A closed-cycle helium cryostat was used to cool the crystals from room temperature down to 16 K. The temperature was controlled within an accuracy of $\pm 0.5$ K. In order to avoid sample-heating effects, we chose a cylindrical lens to focus the incident beam on the sample.

To achieve a signal-to-noise ratio of more than 100, we set the slit width of the spectrometer to 50 $\mu$m. For slit widths below 50 $\mu$m, the signal-to-noise ratio was so small that we could not measure the linewidths of some phonon modes with sufficient accuracy. The measured low-frequency phonon lines of $TlGaS_2$ crystals are so narrow that even with the indicated slit widths, one has to correct for the finite instrument resolution. The width of the response function of the spectrometer was determined by measuring the linewidth of the laser with the same slit openings as in the Raman experiment. An instrumental linewidth of 0.33 $cm^{-1}$ was used in the analysis that follows. The observed peak is a convolution of the Lorentzian shape of the actual phonons with the response function of the spectrometer, which was considered to be Gaussian. To make the deconvolution, we first fit a Voigt profile to our experimental peaks. Then, we calculate the Lorentzian linewidth by using the fitted width of the Voigt profile and the experimentally determined width of spectrometer response function.

## III. RESULTS AND DISCUSSION

### 1. Temperature Dependence of Mode Frequencies

Raman scattering spectra of $TlGaS_2$ at 16 and 300 K are shown in Fig. 2. Fifteen and nineteen Raman lines are observed in the 300- and the 16-K spectra, respectively. Shifts and the broadening of the Raman-active modes with increasing temperature are seen. At low temperatures, all phonon lines are clearly resolved, but at elevated temperatures some closely spaced Raman lines are not resolved in the unpolarized spectra because of temperature-induced broadening.

The phonon spectra of $TlGaS_2$ layered crystals exhibit the typical features of vibrational spectra of molecular crystals, namely, the presence of low-frequency translational modes of the system consisting of $Ga_4S_6$ units and Tl atoms (interlayer vibrations, vibrations of Tl atoms,

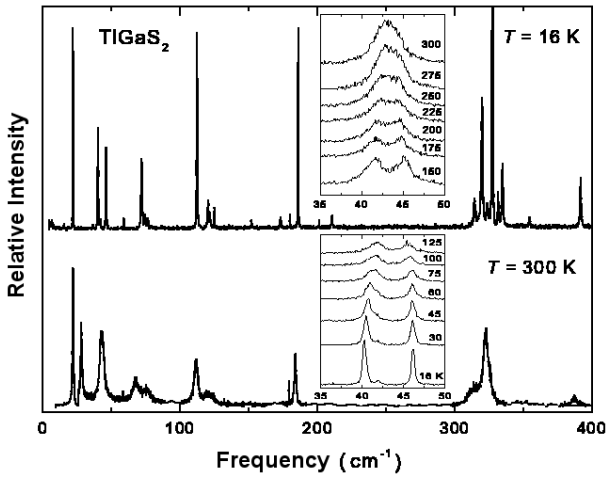


Fig. 2. Raman spectra of the $TlGaS_2$ crystal at $T = 16$ and 300 K. The insets show the extended parts of the Raman spectra in the range of 35 - 50 $cm^{-1}$ at different temperatures.

Table 1. Frequency, frequency shift, temperature slope, and degree of linewidth broadening for Raman-active modes of a $TlGaS_2$ crystal.

| $\nu_{300K}$ ($cm^{-1}$) | $\nu_{300K} - \nu_{16K}$ ($cm^{-1}$) | $[(\partial\nu/\partial T)/\nu]$ ($10^{-5}$ $K^{-1}$) | $(\Gamma_h - \Gamma_l)/\Gamma_l$ |
|---|---|---|---|
| 42.6 | 2.3 | 19.0 | 7.9 |
| 44.0 | −2.1 | −16.8 | 8.8 |
| 67.7 | −4.3 | −22.4 | 8.6 |
| 183.9 | −2.1 | −4.0 | 5.3 |
| 313.0 | −6.9 | −7.7 | 5.2 |
| 322.4 | −5.0 | −5.4 | 6.3 |
| 325.0 | −9.7 | −9.9 | 3.3 |
| 387.1 | −4.6 | −4.2 | 3.6 |

and vibrations of Tl atoms and $Ga_4S_6$ units) and high-frequency "intramolecular" modes of the $Ga_4S_6$ units. The Raman spectra of $TlGaS_2$ crystals in this work at ambient conditions are in good agreement with those of previous studies [4, 5, 17, 18]. At low temperatures, the measured linewidths of low-frequency modes (22.0 and 28.1 $cm^{-1}$) were comparable to the instrumental linewidth. Therefore, we did not analyze the temperature dependence of these modes. We analyzed in detail the temperature dependence of eight strong Raman-active modes. The frequencies of these modes measured at ambient conditions are given in Table 1, along with other relevant quantities and parameters that are discussed below. The three lower-frequency lines correspond to the interlayer modes (42.6 and 67.7 $cm^{-1}$) and vibrations of Tl atoms (44.0 $cm^{-1}$) while the five higher-frequency lines ($\nu \geq 183.9$ $cm^{-1}$) correspond to the intralayer modes. There is large difference between the mode Grüneisen parameters ($\gamma$) for the low-frequency translational (7.3 - 24.3) and the high-frequency "intramolecular" (1.3 - 3.0) modes of $TlGaS_2$ layered crystals [5]. The difference in the mode Grüneisen parameters represents the difference in the translational and "intramolecular" restoring forces. The frequency shifts of $TlGaS_2$ Raman modes in the temperature range 16 - 300 K were found to be from 2.1 to 9.7 $cm^{-1}$ for different modes. The reduced slopes $[(\partial\nu/\partial T)/\nu]$ for all modes are given in Table 1, and show that the values for the high-frequency intralayer modes are almost three times smaller than those of the interlayer modes, thus confirming the stronger bonding (compared to the interlayer modes) within the layers.

The frequencies of the Raman lines observed were plotted against temperature and nearly all showed a normal softening with increasing temperature. The one exception was the interlayer mode with a frequency of 42.6 $cm^{-1}$, which showed hardening with increasing temperature (see Fig. 2, insets). In this mode, entire layers are involved in the vibrations. According to Ref.17, in $TlGaS_2$ crystals, there are two interlayer modes. One of them is the compressional mode $B_g$ (relative displacements of the layers parallel to the $c$-axis) with a frequency of 67.7 $cm^{-1}$ and a force constant of 92.1 N/m. The second is the shear mode $A_g$ (relative displacements of the layers perpendicular to the $c$-axis) with a frequency of 42.6 $cm^{-1}$ and a force constant of 36.0 N/m. The frequencies of these interlayer modes demonstrate quite different behaviors with temperature. The compressional mode with a frequency of 67.7 $cm^{-1}$ exhibits the usual softening ($\Delta\nu = -4.3$ $cm^{-1}$) with increasing temperature from 16 to 300 K while the shear mode with a frequency of 42.6 $cm^{-1}$ shows hardening ($\Delta\nu = +2.3$ $cm^{-1}$) (see Fig. 2, insets). This different behavior may be associated with the differences in force constants (92.1 and 36.0 N/m) and the mode Grüneisen parameters (24.3 and 7.3) for the compressional and the shear modes, respectively.

Similar anomalous behaviors with slight increases in frequencies were observed for the Raman-active modes at 146.3 and 1060 $cm^{-1}$ in $GaPO_4$ and at 1112 $cm^{-1}$ in $AlPO_4$ chain crystals [19]. Such dependencies have also been reported for two infrared-active TO modes (364 and 495 $cm^{-1}$) in $\alpha$-quartz and are associated with weak hardening of these phonons with volume expansion [20].

As representative examples, the frequency versus temperature plots (open squares) for two modes are given in Figs. 3 and 4, one for the interlayer mode at 67.7 $cm^{-1}$ and the other for the intralayer mode at 322.4 $cm^{-1}$. The phonon frequency shift with temperature can be described by the expression [8–12]

$$\nu(T) = \nu_0 + \Delta_1(T) + \Delta_2(T), \quad (1)$$

where $\nu_0 + \Delta_2(0)$ is the Raman frequency as the temperature approaches 0 K, $\Delta_1(T)$ represents the volume dependence of the frequency due to the thermal expansion of the crystals, and $\Delta_2(T)$ specifies the contribution of anharmonic coupling to phonons of other branches.

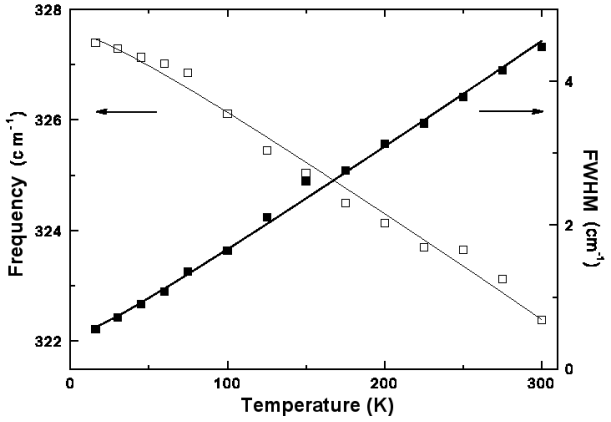


Fig. 3. Temperature dependencies of the translational mode frequency 67.7 cm$^{-1}$ (open squares) and linewidth (solid squares) in the $TlGaS_2$ crystal. The solid curves give the theoretical fits using Eqs. (1)-(3) for the frequency and Eq. (4) for the linewidth.

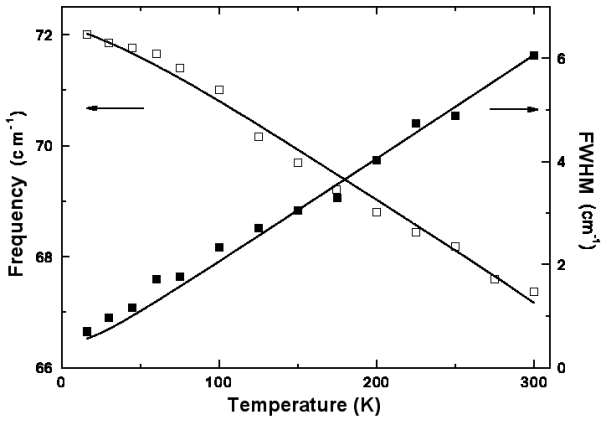


Fig. 4. Temperature dependencies of the "intramolecular" mode frequency 322.4 cm$^{-1}$ (open squares) and linewidth (solid squares) in the $TlGaS_2$ crystal. The solid curves give the theoretical fits using Eqs. (1)-(3) for the frequency and Eq. (4) for the linewidth.

$\Delta_1(T)$ can be written as

$$\Delta_1(T) = \nu_0 \left[ \exp(-3\gamma \int_0^T \alpha(T')dT') - 1 \right], \qquad (2)$$

where $\alpha(T)$ is the coefficient of the linear thermal expansion. In general, the purely anharmonic contribution to the frequency shift can be modeled as

$$\Delta_2(T) = A \left[ 1 + \frac{1}{e^{x_1} - 1} + \frac{1}{e^{x_2} - 1} \right], \qquad (3)$$

which represents the optical phonon coupling to two different phonons (three-phonon processes). Here, $A$ is the anharmonic constant, $x_1 = hc\nu_1/k_BT$, and $x_2 = hc\nu_2/k_BT$ . In the present study, the experiments were carried out at temperatures below the Debye temperature of the $TlGaS_2$ crystal ($\theta_D = 400$ K) [3]. Thus, the three-phonon process is dominant, and the higher order processes can be neglected.

Table 2. Parameters (in cm$^{-1}$) for fitting the temperature dependencies of the Raman-active mode frequency and linewidth of the $TlGaS_2$ crystal.

| $\nu_0$ | $\nu_1$ | $\nu_2$ | A | C |
|---|---|---|---|---|
| 40.2 | 20.1 | 20.1 | 0.16 | 0.20 |
| 46.2 | 23.1 | 23.1 | −0.02 | 0.17 |
| 72.2 | 36.1 | 36.1 | −0.05 | 0.52 |
| 186.4 | 164.0 | 22.4 | −0.19 | 0.11 |
| 321.8 | 151.8 | 70.0 | −1.56 | 1.78 |
| 328.0 | 301.1 | 26.9 | −0.43 | 0.53 |
| 336.7 | 276.7 | 60.0 | −2.11 | 1.02 |
| 392.7 | 332.7 | 60.0 | −0.71 | 0.91 |

The frequency shifts for the Raman modes of $TlGaS_2$ crystals were fitted by means of Eqs. (1)-(3) by using the experimental values of $\gamma$ and $\alpha(T)$ for $TlGaS_2$ [5,21] with $A, \nu_0, \nu_1$, and $\nu_2$ as adjustable parameters, keeping the sum $\nu_1 + \nu_2 = \nu_0$ a constant (energy conservation). For all modes, the agreement between the theoretical and the experimental dependencies was found to be good. Figures 3 and 4 show this agreement for two representatives of translational and "intramolecular" modes with frequencies of 67.7 and 322.4 cm$^{-1}$, respectively. The resulting parameters for all modes are shown in Table 2. Generally, if the decay channels of the phonon modes are to be identified, all possible interactions should be considered for the decay processes, taking into account the phonon dispersion curves. Unfortunately, the lack of phonon dispersion curves for $TlGaS_2$ does not allow confirmation of the decay channels determined by fitting Eqs. (1)-(3) to experimental data.

We have also calculated separately the thermal-expansion contribution [$\Delta_1(T)$] from Eq. (2) and the purely anharmonic contribution [$\Delta_2(T)$] from Eq. (3) to the line shift for Raman modes of $TlGaS_2$ crystals by using the adjusted values of parameters $A, \nu_0, \nu_1$, and $\nu_2$ obtained above. The variations of $\Delta_1(T)$ and $\Delta_2(T)$ for all modes are given in Fig. 5, together with the experimental frequency shifts. We notice that all translational modes display a downward volume-induced shift. The modes at 44.0 and 67.7 cm$^{-1}$ also show a downward shift due to the anharmonic effect, which is weaker (seven and eight times, respectively) than the volume-induced one. For the mode at 42.6 cm$^{-1}$, which shows hardening with increasing temperature, the shifts caused by the two effects have opposite signs. However, in this mode, the shift due to the anharmonic effect is greater (four times), in absolute terms, than the volume-induced shift.

Turning our attention to the intralayer modes, we notice that in all modes the contributions of the volume-induced and the anharmonic shifts have the same sign

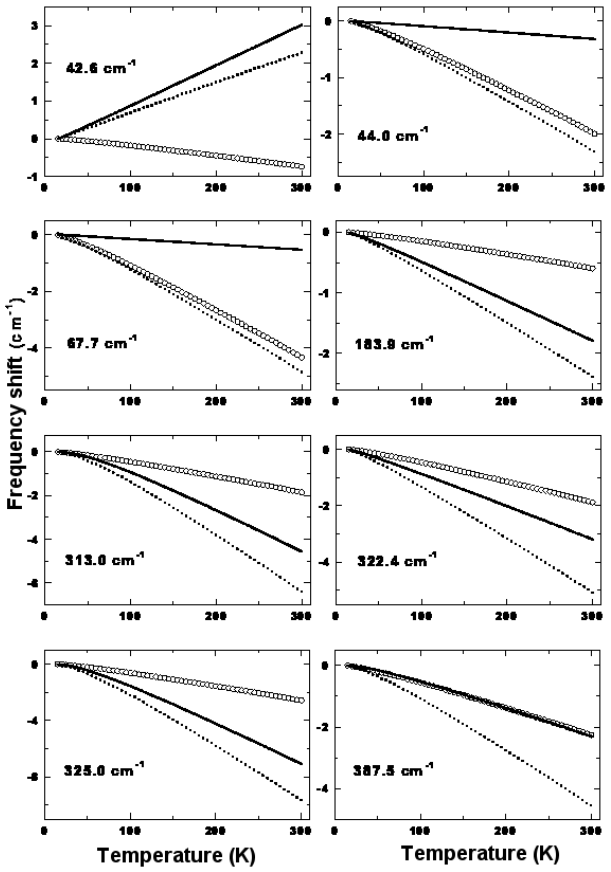


Fig. 5. Temperature dependencies of the experimental Raman frequency shifts (dotted curves) and of the volume-induced (open circles) and anharmonic (solid curves) contributions to the frequency shifts.

(negative), the latter being greater. Only in the mode at 387.5 $cm^{-1}$ are both contributions comparable. According to the model proposed by Weinstein and Zallen [22], the thermal expansion (volume) effects dominate, as the vibrational modes involve atomic species with non-overlapping electronic configurations. In contrast, when substantial electronic overlap exists, the volume effect is relatively reduced so the shifts induced by the two effects become comparable, with the anharmonic contribution being higher than the volume one in most cases. Our experimental data are in accordance with this model. As we mentioned above, in the translational modes, weak bonds are involved in the restoring forces. On the other hand, in the "intramolecular" modes, the restoring forces are due to the strong intralayer gallium-sulfur bonds (see Fig. 1).

### 2. Temperature Dependence of Mode Linewidths

The linewidth of the $TlGaS_2$ phonons was studied systematically as a function of temperature in the range of 16 - 300 K. The corrected linewidths of the 8 Raman modes observed at room temperature were found to be 2.8, 2.5, 6.1, 1.3, 6.4, 4.2, 4.1, and 4.1 $cm^{-1}$. The linewidths of all optical modes are found to increase with temperature. The broadening of the phonon lines is due to anharmonicity of the lattice vibrations. The presence of anharmonic forces in a crystal leads to interactions between the harmonic normal modes. These interactions produce temperature-dependent lifetimes for the normal modes.

We consider the ratio $(\Gamma_h - \Gamma_l)/\Gamma_l$ as a quantitative measure of the line broadening, where $\Gamma_h$ and $\Gamma_l$ represent the linewidth at the highest (300 K) and the lowest (16 K) temperatures of the measurement. The values of this ratio for all modes are shown in Table 1. It is apparent that the linewidth broadening is smaller for the high-frequency intralayer modes and that this result is anticipated because of the stronger binding of atoms within the layers.

The temperature dependence of the phonon linewidth can be described as follows [8,10,12,14]:

$$\Gamma = C\left[1 + \frac{1}{e^{x_1} - 1} + \frac{1}{e^{x_2} - 1}\right], \qquad (4)$$

where $C$ is the broadening of the phonon line due to the cubic anharmonicity at absolute zero (the decrease in phonon lifetime, $\tau$, due to the decay of the optical phonon into two different phonons). Figures 3 and 4 shows also the linewidth broadening with increasing temperature (closed squares) for two representative modes, translational and "intramolecular", with frequencies 67.7 and 322.4 $cm^{-1}$, respectively. The experimental data for the phonon linewidths of the Raman-active modes of $TlGaS_2$ crystals were fitted by means of Eq. (4) with $C, \nu_1$, and $\nu_2$ as fitting parameters, keeping the sum $\nu_1 + \nu_2 = \nu_0$ constant. We obtained quantitative agreement between the calculated curves and the experimental data (Figs. 3 and 4). The fitting parameters for all Raman modes are listed in Table 2.

We obtained a good fit to the experimental data for the low-frequency modes with $\nu_1 = \nu_2$ (see Table 2). For many semiconductors, a reasonable fit to the temperature dependence of the linewidth broadening is obtained using $\nu_1 = \nu_2$ [10, 12–14, 23]. The existence of a dominant contribution to the linewidth broadening for $\nu_1 = \nu_2$ has been confirmed by *ab-initio* calculations for diamond [24], InP and AlAs [15], although for Ge and Si [24] and GaAs and GaP [15], $\nu_1 = 2\nu_2$ seems to give a better approximation to the linewidth versus temperature data.

## IV. CONCLUSIONS

The temperature behaviors of the frequencies and the linewidths of Raman-active modes in $TlGaS_2$ crystals are well described by anharmonic (phonon-phonon coupling)

and volume (thermal expansion) contributions. Cubic (three-phonon) processes with energy conservation are responsible for the anharmonic contributions to the frequency shift and the broadening of the phonon lines. The interlayer mode at 42.6 $cm^{-1}$ was found to exhibit a frequency change toward high frequencies as the temperature was raised from 16 to 300 K.

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